

Catalytic Hydroliquefaction of Coal Using
Molybdenum and Iron-Promoted Catalysts

Larry L. Anderson, W.H. Yuen, J. Jaturapitpornsakul,
Department of Chemical and Fuels Engineering
D. Sommerfeld, and E. M. Eyring,
Department of Chemistry
University of Utah
Salt Lake City, Utah 84112

Keywords: coal, hydroliquefaction, catalytic coal liquefaction.

INTRODUCTION

Coal has been liquefied to volatile liquid products by a variety of methods but the feasibility of this method of producing synthetic liquid fuels depends on conversion without extreme reaction conditions. To react coal at milder than those used in the German plants (high pressures and temperatures) requires the application of catalysts which permit reaction at reasonable rates and conversion levels. Iron has been used in many catalytic liquefaction processes because of its low cost and low environmental impact. In this study several iron catalysts and combinations tested on bituminous and subbituminous coals. The iron catalysts used were mostly ineffective at significantly increasing the fraction of coal converted to liquids. However, iron was found to migrate throughout the coal particles during the reaction holding the promise that an effective iron catalyst may still be a possibility.

Catalytic reactions were done without solvents or vehicle oils to avoid the complexity of product characterization and to simplify the procedure.

COALS AND EXPERIMENTAL CONDITIONS

Several coals from the Argonne Premium coal sample bank and the Penn State sample bank were used in the dry hydroliquefaction experiments. These included: Blind Canyon, Utah; Elkhorn, Illinois; Hiawatha, Utah; Pittsburgh, Pennsylvania; Wyodak, Wyoming; Illinois #6, Illinois; and Lewiston-Stockton, West Virginia coals. The proximate, ultimate, and maceral analyses have been given previously for these coals.¹ The experimental procedure consisted of taking the coal, either -100 mesh (Penn State - DECS-6) or -60 mesh (Argonne Samples) and impregnating the catalyst, if any, from aqueous solution onto the surface of the coal. The mixture was then dried for 4 hours at 60°C. When promoters were used with Mo catalysts the Mo was impregnated first, the mixture dried; the promoter was then added and the mixture dried again. The coal and any catalyst were placed in a tubing reactor, sealed, pressurized with hydrogen, and attached to a shaking mechanism. The reactor was then immersed into a sand bath heated to the reaction temperature. Reactions were conducted usually for one hour with shaking at 160 rpm. For some experiments the coals were first extracted with tetrahydrofuran (THF) or were demineralized with HCl and HF. Experiments were run with no catalyst or with one or more of the following: ammonium tetrathiomolybdate $[(\text{NH}_4)_2\text{MoS}_4]$, iron (III) chloride hexahydrate $[\text{FeCl}_3 \cdot 6\text{H}_2\text{O}]$, nickel (II) chloride hexahydrate $[\text{NiCl}_2 \cdot 6\text{H}_2\text{O}]$, nickel (II) nitrate $[\text{Ni}(\text{NO}_3)_2]$, ammonium ferric sulfate $[\text{NH}_4\text{Fe}(\text{SO}_4)_2]$ (AFS), ferrocene $[\text{C}_{10}\text{H}_{10}\text{Fe}]$, ferric citrate. After the reaction the reactor was taken out of the sand bath, quenched, and the gases vented for analysis. The liquids and solids were extracted with THF. Conversion was defined as:

$$\text{Conversion} = 100 - \frac{(\text{weight of maf THF-insolubles in product})}{\text{weight of maf coal charged}} \times 100$$

RESULTS AND DISCUSSION

Some preliminary experiments were done to determine the effects of different impregnation methods, reaction time, and hydrogen pressure on the liquefaction yields. Impregnation by incipient wetness (catalyst solution

just the entire coal surface) or ultrasonic treatment¹ (excess solution, with application of ultrasonic energy for two hours) gave essentially the same results. Liquefaction yields after 1 hour, 2 hours, and 3 hours were determined. Hydrogen pressures of 1000, 2000, and 3000 psi (at reaction temperature) were used.

Since similar results were obtained for all the coals tested most of the data reported here are for Blind Canyon, Utah coal. Some results for runs at 350, 400, and 425°C will be reported although other runs were done at higher temperatures. Above 400°C reactions gave significant gas conversion and corresponding reduced liquid yields.

Soxhlet extraction of Blind Canyon (BC) coal gave 19.9 per cent THF-soluble liquids. Hydroliquefaction without catalyst gave approximately 22 per cent liquids at 350° and 30 per cent at 400°. Several iron catalysts were tested for liquefaction effectiveness. Table 1 shows the liquid yields for Pittsburgh #8 coal at 350 and 450°. Molybdenum catalysts gave higher liquefaction yields than any other catalysts we tested in dry hydroliquefaction experiments. Figure 1 gives results for Mo (as ammonium tetrathiomolybdate) hydroliquefaction of BC coal at 400°C. The improvement of liquid yields from less than 30 per cent without catalyst to near 80 per cent with only 0.05 per cent Mo was dramatic but we also wanted to determine if further improvements could be obtained by using iron or nickel as promoters for the molybdenum catalyst.

The main results of testing iron and nickel as promoters are shown in figures 2 and 3. Both iron as iron chloride and nickel as nickel chloride were active as promoters even at low concentrations i.e. 0.01 per cent. The iron was slightly better than nickel at 350° while the reverse was true at 400°C (Figure 4).

To determine the effectiveness of our impregnation methods and to locate the catalyst materials after the reaction, we utilized electron probe microanalysis (EPMA)³. With this technique one can determine the dispersion of certain elements. To do this the insoluble product is embedded in a resin block using Petropoxy 154 and polished on a Syntrol diamond paste polisher. Samples are sputter-coated with carbon to minimize charging in the electron microscope. Characteristic X-rays are collected for iron, nickel, molybdenum, sulfur and other elements with an energy dispersive spectrometer detector (CAMECA Model SX-50 detector, Courbevoie Cedex, France). Visual images of the samples are made from secondary electron and back-scattered electron images of the sample. X-ray data analysis is carried out with a Digimap program. Magnification of the samples is typically 2000 yielding a Digimap area of about 45 microns by 45 microns for each micrograph.

Figure 5 shows a coal particle in the center with sulfur accumulated around the particle (A). The Mo response in B is similar. In Figure 6A the visual image shows a coal particle while 6B shows that the dispersion of iron after reaction is uniform throughout the coal particle.

The products of the hydroliquefaction reaction were char, liquids (defined as THF-soluble), and gases. The gases were minor (2 per cent of the maf coal at 350°, 12 per cent at 400°, and 16 per cent at 425°C) products and were composed mostly of carbon dioxide and methane. As the temperature increased the fraction of the gases that were methane, ethane, and propane increased while that for carbon dioxide decreased. The liquid products were quite similar, with average molecular weights between 240 and 270. When the reaction time was increased to 3 hours the average molecular weight increased slightly to about 310. Table 2 gives compositional information on representative liquids produced from BC coal at 350°C and 400°C. ¹³C nuclear magnetic resonance spectroscopy of the liquids produced in experiment MS-BC #28 showed that the aromaticity was 0.64, the aliphatic fraction was 0.32 and that the average molecular weight per cluster was 326. This was similar to results obtained for other liquid products.

SUMMARY AND CONCLUSIONS

High liquid yields can be obtained by dry hydroliquefaction when an active catalyst is applied, even at relatively mild conditions (2000 psi, hydrogen and 400°C, for one hour). Molybdenum sulfide was found to be the most effective for the conditions tested and was used in concentrations of 0.05 per cent or less (weight of Mo as per cent of maf coal). Iron and nickel were found to be active as promoters for liquefaction using Mo catalyst at 350° and 400°C. Increasing hydrogen pressure resulted in higher yields of liquid product.

ACKNOWLEDGEMENT

The authors would like to thank the U.S. Department of Energy through the Consortium for Fossil Liquefaction Science and the State of Utah who financially supported this research.

REFERENCES

1. Anderson, L.L. and J. Jaturapitpornsakul, Proc.Sixth Ann. Int. Pittsburgh Coal Conf. 1989, 1, 104-112.
2. Wann, J.P., 1987, M.S. Thesis University of Utah, Salt Lake City, Utah.
3. Sommerfeld, D.A., J. Jaturapitpornsakul, L.L. Anderson, and E.M. Eyring, 1992, Preprints Div. Fuel Chem., Am. Chem. Soc., 37, No. 2, 749-755.

TABLE 1. Hydroliquefaction of Pittsburgh #8 (HVB) coal using several iron catalysts.

Run No.	Catalyst	Temp. °C	THF Insol.	% of maf coal
				THF Soluble (Liquefaction %)
FP-PT #5	- none -	450	65	14
FRC-PT #1	Ferrocene	450	53	28
FRC-PT #2	Ferrocene	350	67	33
FCT-PT #1	Ferric Citrate	450	42	33
FCT-PT #2	Ferric Citrate	350	62	38

Table 2. Composition of Liquid Products from the hydroliquefaction of Blind Canyon coal at 400°C and 350°C at 2000 psi hydrogen and 1 hour reaction time (except as noted otherwise).

Run #		C	H	N	S	O (diff)	H/C	O/C
400°C								
DECS-6	(dmmf - mod. Parr)	81.72	6.22	1.56	0.40	10.10	0.91	0.093
MS-BC #6	0.05% Mo	85.48	6.91	1.59	0.29	5.75	0.97	0.051
MS-BC #7	0.03% Mo	85.36	6.91	1.49	0.32	5.92	0.97	0.052
MS-BC #28	0.03% Mo, 3 hour	86.31	7.34	1.47	0.16	4.73	1.02	0.041
MS-BC #10	0.01%Ni+0.03%Mo	85.42	7.01	1.51	—	5.76	0.98	0.051
MS-BC #12	1.00% Fe	85.57	7.13	1.72	—	5.34	1.01	0.047
MS-BC #18	0.20% Ni	84.93	6.97	1.55	—	6.36	0.98	0.056
350°C								
BC (Argonne)	(dmmf - mod. Parr)	81.32	5.81	1.59	0.40	10.88	0.86	0.100
MS-BCA #3	0.05% Mo	82.36	7.08	1.20	—	9.06	1.03	0.082
MS-BCA #7	1.00%Fe+0.05%Mo	79.69	6.66	1.17	—	12.19	1.00	0.115
MS-BCA #9	1.00%Ni	81.43	7.14	1.23	—	9.91	1.05	0.091

FIGURE 1.. Hydroliquefaction of Blind Canyon coal (DECS-6) at 400°C, 2000 psi hydrogen for 1 hour.

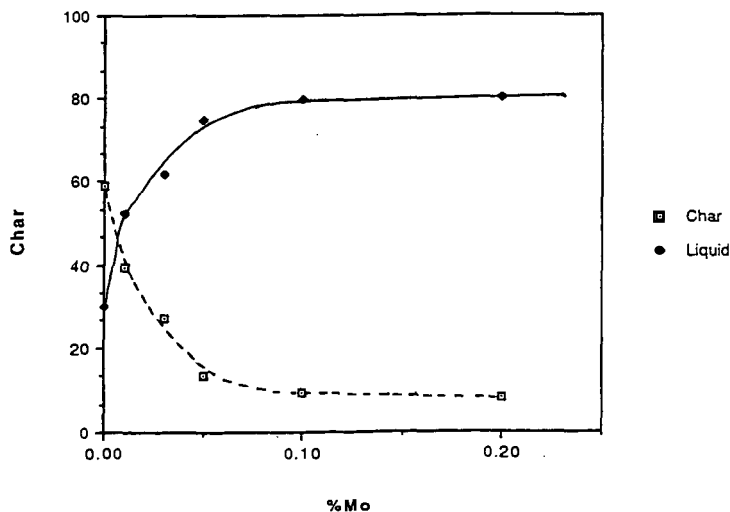


FIGURE 2. Hydroliquefaction of Blind Canyon coal (Argonne) at 2000 psi hydrogen for 1 hour at 350°.

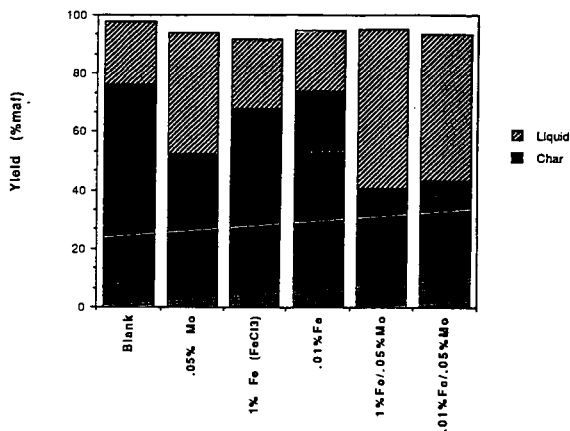


FIGURE 3. Hydroliquefaction of Blind Canyon coal (DECS-6) at 350°C for 1 hour with several different catalysts and combinations.

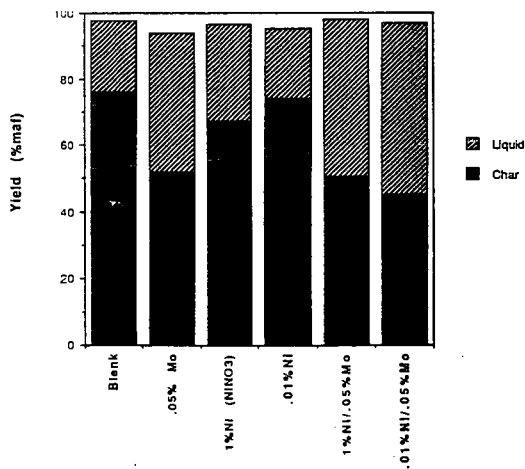


FIGURE 4. Hydroliquefaction of Blind Canyon coal at 400°C for 1 hour at 2000 psi hydrogen using iron or nickel as promoters for molybdenum catalyst (0.03% Mo).

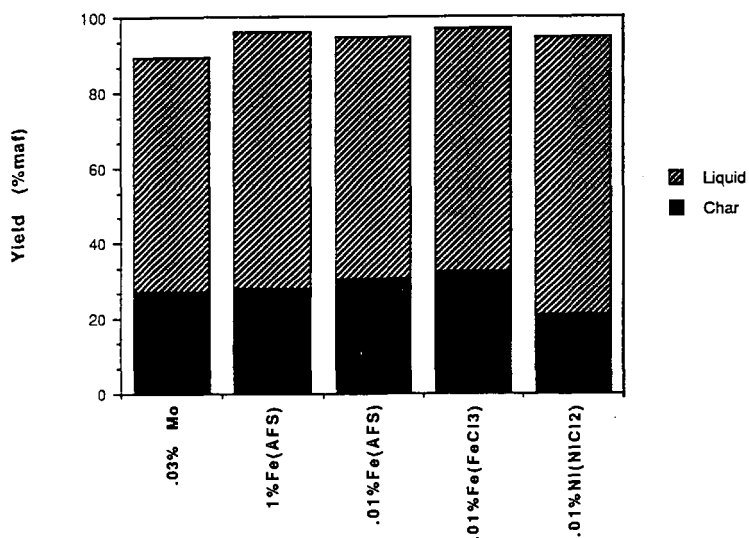


FIGURE 5. Electron Probe Microanalysis (EPMA) showing the dispersion of sulfur (A) and Molybdenum (B) for a Blind Canyon coal particle after impregnation with 1 per cent iron and 1 per cent molybdenum but before reaction.

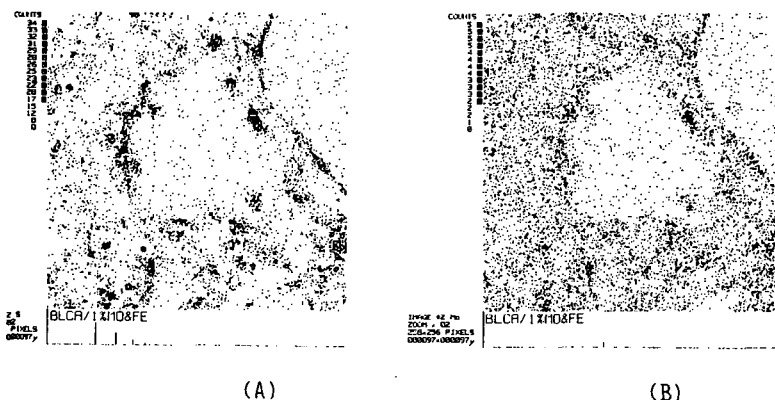


FIGURE 6. Electron Probe Microanalysis (EPMA) showing a Blind Canyon coal particle (center) after hydroliguefaction reaction. The catalyst used was 1 per cent iron and 1 per cent molybdenum. (A) shows a visual image of the coal particle and (B) shows the evenly dispersed iron through the coal particle.

